# PATENT SPECIFICATION

(11) 1402697

1402697

(21) Application No. 50278/73 (22) Filed 29 Oct. 1973

(31) Convention Application No. 315054 (32) Filed 14 Dec. 1972 in

(33) United States of America (US)

(44) Complete Specification published 13 Aug. 1975

(51) INT CL² C10M 3/14 3/20 3/26

(52) Index at acceptance

C5F 482 531 536 591 594 610 672 673 674 733

(19)


## (54) SYNTHETIC AIRCRAFT TURBINE OIL

(71) We, TEXACO DEVELOPMENT CORPORATION, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of 135 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention is concerned with a lubricating oil composition for a gas turbine or jet engine. Gas turbine aircraft engines are operated under extreme environmental conditions. External atmospheric temperatures are generally below zero and internal engine temperatures are 400—500°F or above. These operating conditions put severe stresses on the lubricating oil, so much so that the most advanced mineral lubricating oil compositions cannot be employed in gas turbine engines.

Synthetic ester base lubricating oil compositions containing a critically balanced blend of additives are being employed for lubricating gas turbine engines. These ester base oils are usable over a wide temperature range and exhibit good thermal stability, anti-wear, load-carrying and anti-oxidation properties.

With the advent of advanced, more powerful gas turbine engines, higher thermal and oxidative stresses are imposed on the lubricating oil composition. The present invention is directed to an improved high load carrying synthetic ester base lubricating oil composition having improved deposit control properties.

U.S. Patent No. 3,330,763 discloses a synthetic lubricating oil composition having improved load-carrying properties employing an ester base oil containing in combination an ammoium thiocyanate and a cyclic amine compound of the type represented by phenyl-alpha-napthyl-amine.

British Patents No. 1,180,386 to 1,180,389 disclose synthetic lubricating oil compositions containing, *inter alia* a copper passivator, which may be of the Azole type, or a condensation product of a salicylaldehyde and a hydrazine derivative, as well as amine antioxidants and varies other additives.

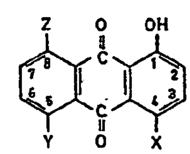
The synthetic lubricating oil composition of this invention having improved deposit control properties comprises a major proportion of an aliphatic ester base oil having lubricating properties formed from the reaction of pentaerythritol, a polypentaerythritol or trimethylolpropane and an organic monocarboxylic and having from 2 to 18 carbon atoms per molecule containing (A) from 0.01 to 2.5 weight percent of an ammonium thiocyanate represented by the formula:

$$R\overset{+}{N}R'R''R'''\overset{-}{S}CN$$

in which R is a hydrocarbyl or amino-substituted hydrocarbyl group having from 1 to 30 carbon atoms or a radical having the formula:

$$-R''''\underset{R'''}{\overset{R'}{N}}R''SCN$$

in which R'''' is a bridging polymethylene radical having from 2 to 4 carbon atoms, and R', R'' and R''' represent hydrogen or a hydrocarbyl group having 1 to 30 carbon atoms, (B) from 0.4 to 2 weight percent of a polyhydroxy-substituted anthraquinone represented by the formula:




in which X, Y and Z each represent hydrogen or a hydroxyl group and at least one of these is a hydroxyl group, and (C) from 0.001 to

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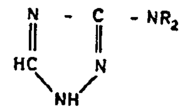
0.1 weight percent of a 3 - amino - 1H - 1,2,4 - triazole having the formula:



in which R is hydrogen or an alkyl radical having from 1 to 3 carbon atoms.

This invention is based on the discovery that an ester base lubricating oil composition containing the fore-going additive combination has superior oxidative stability. While certain ester base lubricating oil compositions containing ammonium thiocyanates in combination with cyclic amines have effective load-carrying properties, the present highly specific additive combination in a particular fluid formulation provides a surprising and outstanding improvement in oxidative stability and deposit control.

The base fluid component of the lubricant of the invention is an ester-base fluid prepared from pentaerythritol, a polypentaerythritol or trimethylolpropane and a $C_2$—$C_{18}$ monocarboxylic acid or a mixture of such acids. Polypentaerythritols include dipentaerythritol, tripentaerythritol and tetrapentaerythritol.

The hydrocarbyl monocarboxylic acids which are used to form the ester-base fluid include the straight-chain and branched-chain aliphatic acids, cycloaliphatic acids and aromatic acids, and also mixtures of these acids. The acids employed have from 2 to 18 carbon atoms per molecule, the preferred members having from 5 to 10 carbon atoms. Examples of suitable acids are acetic, propionic, butyric, valeric, isovaleric, caproic, decanoic, cyclohexanoic, naphthenic, benzoic, phenylacetic, tertiary-butylacetic and 2-ethylhexanoic acids.

In general, the acids are reacted in proportions leading to a completely esterified pentaerythritol, polypentaerythritol or trimethylolpropane with the preferred ester bases being the pentaerythritol tetraesters. Examples of commercially available tetraesters include pentaerythritol tetracaproate, which is prepared from purified pentaerythritol and crude caproic acid containing other $C_5$—$C_{10}$ monobasic acids. Another suitable tetraester is prepared from a technical grade pentaerythritol and a mixture of acids comprising 38 percent valeric, 13 percent 2-methyl-pentanoic, 32 percent octanoic and 17 percent pelargonic acids. Another effective ester is the triester of trimetholopropane in which the trimetholopropane is esterified with a monobasic acid mixture consisting of 2 percent valeric, 9 percent caproic, 13 percent heptanoic, 7 percent octanoic, 3 percent caprylic, 65 percent pelargonic and 1 percent capric acids. Trimethylolpropane tripheptanoate, trimethylolpropane pentanoate and trimethylolpropane hexanoate are also suitable ester bases.

The ester base comprises the major portion of the fully formulated synthetic ester base lubricating oil composition. The ester base normally constitutes at least 90 percent of the lubricating oil composition and generally will comprise from 90 to 98 percent of the lubricant.

The ammonium thiocyanate component of the lubricating oil composition of the invention is represented by the formula:

$$R\overset{+}{N}R'R''R'''\overset{-}{SCN}$$

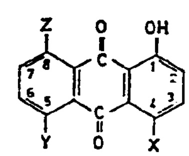
in which R is a hydrocarbyl or amino-substituted hydrocarbyl group having from 1 to 30 carbon atoms or a radical having the formula:

$$-R''''\overset{R'}{\underset{R'''}{N}}R''SCN$$

in which R'''' is a bridging polymethylene radical having from 2 to 4 carbon atoms, and R', R'' and R''' may be alkyl, cyclo-alkyl, aryl or mixed hydrocarbyl groups. In the preferred compounds, R is an aliphatic hydrocarbon radical having from 8 to 22 carbon atoms and R', R'' and R''' are hydrogen or an aliphatic hydrocarbon radical having from 1 to 4 carbon atoms.

Effective ammonium thiocyanates include bis - (2 - ethylhexyl) - ammonium thiocyanate, tert. - $C_{16-22}$ alkyl-ammonium thiocyanate, sec.-$C_{10-14}$ alkylammonium thiocyanate, tert.-octylammonium thiocyanate, n-dodecylammonium thiocyanate, tert.-$C_{12-14}$-alkylammonium thiocyanate, nonylammonium thiocyanate, laurylammonium thiocyanate, stearylammonium thiocyanate, dimethyl-2-ethylhexylammonium thiocyanate, dibutyloctylammonium thiocyanate, N,N'-di-(t-octyl)-1,2-ethanediammonium thiocyanate and N,N') - di - (t - $C_{18-22}$ alkyl - 1,2 - ethanediammonium thiocyanate. The ammonium thiocyanate is normally employed at a concentration from 0.01 to 2.5 weight percent with the preferred amount being from 0.05 to 0.5 percent.

Another essential component of the lubricating oil composition is a polyhydroxy-substituted anthraquinone inhibitor represented by the formula:



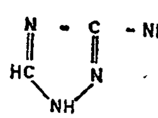
in which X Y and Z each represent hydrogen or a hydroxyl group and at least one of these is a hydroxyl group. It is essential that the polyhydroxy-substituted anthraquinone has the proper structure. This compound must have at least two hydroxyl groups and both of these must be attached to the ring carbon atoms in the *alpha*-position to the quinone ring i.e. or positions 1 and 4, 5 or 8. Additional hydroxyl groups may be present without changing the effectiveness of the noted compounds. Compounds having only one hydroxyl group and compounds having more than one hydroxyl group but with only one on the 1, 4, 5 and 8 carbon positions are not effective in the present invention. The specific polyhydroxy-substituted anthraquinones noted above must be employed with the prescribed ammonium thiocyanate and with the prescribed 3-amino-1H-1,2,4-triazole to provide the improved lubricating oil composition of the invention.

Examples of effective polyhydroxy-substituted anthraquinones include 1,4-dihydroxyanthraquinone, 1,5-dihydroxyanthraquinone, 1,2,4-trihydroxyanthraquinone and 1,2,5,8-tetrahydroxyanthraquinone.

The ineffective hydroxy-substituted anthraquinones include 1-hydroxyanthraquinone, 5-hydroxyanthraquinone, 1,2-dihydroxyanthraquinone and 2,6-dihydroxyanthraquinone.

The effective polyhydroxy-substituted anthraquinone inhibitor is employed in a concentration of from 0.04 to 2.0 weight percent of the lubricating oil composition with the preferred concentration being from 0.05 to 0.25 weight percent. It is essential to observe the lower concentration limit for the inhibitor, since amounts at 0.035 weight percent concentration do not provide the improvements of the invention.

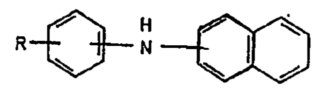
A further essential component of the lubricating oil composition is a 3-amino-1H-1,2,4-triazole having the formula:



in which R is hydrogen or a alkyl radical having from 1 to 3 carbon atoms. Specific members of this class include 3-amino-1H-1,2,4-triazole, 3-methylamino-1H-1,2,4-triazole, 3-ethylamino-1H-1,2,4-triazole and 3-dimethylamino-1H-1,2,4-triazole.

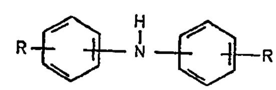
The 3-amino-1H-1,2,4-triazole is employed at a concentration of from 0.001 to 0.1 weight percent amounts, equivalent to 10 to 1000 p.p.m. (parts per million). The preferred concentration is from 0.003 to 0.5 weight percent with the most preferred range being from 0.005 to 0.02 weight percent.

The effectiveness of the lubricating oil compositions of the invention is enhanced by the addition of other additives to the oil composition. Alkyl- or alkaryl-phenyl naphthylamines are highly effective anti-oxidants for synthetic lubricating oils. These compounds are represented by the formula:



in which R is an alkyl or alkaryl radical having from 4 to 12 carbon atoms. This radical can be a straight- or branched-chain alkyl radical with the tertiary alkyl structure being preferred, or it can be an alkaryl radical. The naphthylamine can be either an *alpha*- or *beta*-naphthylamine. Specific effective compounds of this class include N - (*p* - *t* - octylphenyl) - $\alpha$ - naphthylamine, N - (*p* - cumylphenyl) - 6 - cumyl - $\beta$ - naphthylamine, N - (*p* - *t* - octylphenyl) - $\beta$ - naphthylamine and the corresponding *p*-*t*-dodecylphenyl, *p*-*t*-butylphenyl, and *p*-dodecylphenyl-$\alpha$- and -$\beta$-naphthylamines. An effective concentration for this additive is an amount from 0.5 to 2.5 weight percent.

Another effective anti-oxidant for the lubricating oil composition of the invention, which may if desired be used simultaneously with the alkyl- or alkaryl-phenyl naphthylamine, is a dialkyldiphenylamine represented by the formula:



in which R is an alkyl radical having from 4 to 12 carbon atoms. Examples of these amines include p,p'-di-tert.-octyldiphenylamine, didecyldiphenylamine, didodecyldiphenylamine, and dihexyldiphenylamine. p,p'-di-tert.-octyldiphenylamine is the preferred compound and the preferred concentration is from 0.5 to 2.0 percent.

A valuable anti-wear component for a synthetic lubricating oil composition is a hydrocarbyl phosphate, represented by the formula $(RO)_3PO$, in which R is a hydrocarbyl radical having from 2 to 12 carbon atoms. The hydrocarbyl radical can be an alkyl, aryl, alkaryl, cycloalkyl or aralkyl radical of the prescribed carbon number, although radicals having from 4 to 8 carbon atoms are preferred. Effective compounds include tricresyl phosphate, cresyl diphenyl phosphate, triphenyl phosphate, tributyl phosphate, tri-(2-ethylhexyl) phosphate and tricyclohexyl phosphate. These compounds are generally employed in a lubricating oil composition in a concentration of from 0.5 to 5 percent.

The lubricating oil composition of the invention was tested for its marked improve-

ment in deposit control properties in the Alcor Deposition Test and for its resistance to oxidation and particularly reduced corrosivity to copper in the 425°F/48 Hour Oxidation-Corrosion Test. The lubricating oil composition must pass the Alcor Deposition Test in order to qualify against the U.S. Navy's XAS-2354 specification.

The Alcor Deposition Test is described in the foregoing U.S. Navy specification and is designed to determine gas turbine lubricant deposit and degradation characteristics. In this test, the oil is circulated at 300 ml/min. together with humidified air injection at 1000 ml/min. through a heater tube maintained at 550°F. for a period of 48 hours. Initial maximum tube temperature is from 675—700°F. The deposits formed in the tube are weighed or the test is terminated when the tube temperature reaches 900°F.

The 425°F/48 Hr. Oxidation-Corrosion Test is conducted in accordance with Method 5308.4 of Federal Test Method and Standard No. 791a (issued December 31, 1969) exect for modifications to conform to Pratt and Whitney 521-B specifications. The bath temperature is maintained at 425°F±1° Fahrenheit instead of at 250°F and the test is conducted for a period of 48 hours instead of 168 hours as specified in the original test.

The ester base oil employed in preparing the lubricating oil compositions tested below was a technical grade pentaerythritol containing a minor amount of dipentaerythritol esterified with a mixture of fatty acids comprising (in mole percent) approximately 38 percent valeric, 13 percent 2-methyl-pentanoic, 32 percent n-octanoic and 17 percent pelargonic acid and in which the average acid carbon chain length is about 6.5.

This ester base oil had the following properties:

| | |
|---|---|
| Viscosity, cS at 210°F | 5.05 |
| Viscosity, cS at 100°F | 26.0 |
| Viscosity, cS at −40°F | 7683 |
| Viscosity Index | 140 |
| Flash, °F | 505 |

Two Base Fluids were prepared employing the foregoing ester base oil.

Base Fluid A consisted of 1.0 weight percent of p,p'-di-tert.-octyldiphenylamine, 1.5 weight percent of N-(*p*-*t*-octylphenyl)-1-naphthylamine, 2.0 weight percent tricresyl phosphate, 0.1 weight percent *t*-$C_{18}$—$C_{22}$-alkyl-primary amine salt of thiocyanic acid, 0.1 weight percent quinizarin and the balance the ester base referred to above.

Base Fluid B was similar except that it contained 1.5 weight percent of N-4-cumylphenyl)-6-cumyl-2-naphthylamine in place of the N-(*p*-*t*-octylphenyl)-1-naphthylamine.

The results of the Alcor Deposition Test are set forth in Table I below.

TABLE I
Alcor Deposition Test

| Run | Base Fluid | Additive & Conc. | Deposits, mg |
|---|---|---|---|
| 1. | A | none | 11.1 |
| 2. | B | none | 21.0 |
| 3. | A | 3-amino-1H-1,2,4-triazole, 50 ppm | 4.7 |
| 4. | A | 3-amino-1H-1,2,4-triazole, 100 ppm | 4.9 |
| 5. | B | 3-amino-1H-1,2,4-Triazole, 50 ppm | 5.2 |
| 6. | B | 3-amino-1H-1,2,4-triazole, 100 ppm | 8.1 |

The foregoing examples illustrate an unexpected reduction in engine deposits as measured by the Alcor Deposition Test. In the case of Base Fluid A, deposits were reduced by over 50 per cent at concentration levels of 50 and 100 weight parts per million.

In the case of Base Fluid B, deposits were reduced by from 60 to 75 per cent at two different levels of additive concentration.

The results of the Oxidation-Corrosion Test on Copper corrosion are given in Table II below wherein blends containing the additive of the invention are compared to Base Fluid A.

TABLE II

425°F/48-Hour Oxidation-Corrosion Test

| | Blend Identification | | | Metal Weight Change(mg/cm²) | |
|---|---|---|---|---|---|
| Run | Additive | Conc. ppm | TAN INCR. | Cu. | Base Fluid |
| 1 | None | —— | 2.60 | −1.78 | A |
| 2 | 3-Amino-1H-1,2,4-triazole | 50 | 2.45 | −0.49 | A |
| 3 | 3-Amino-1H-1,2,4-triazole | 100 | 1.90 | −0.47 | A |

WHAT WE CLAIM IS:—

1. A synthetic lubricating oil composition comprising a major proportion of an aliphatic ester base oil having lubricating properties formed from the reaction of pentaerythritol, a polypentaerythritol or trimethylolpropane and an organic monocarboxylic acid having from 2 to 18 carbon atoms per molecular containing:

A. From 0.01 to 2.5 weight percent of an ammonium thiocyanate represented by the formula:

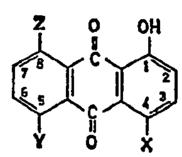
$$R\overset{+}{N}R'R''R'''\overset{-}{S}CN$$

in which R is a hydrocarbyl or an amino-substituted hydrocarbyl group having from 1 to 30 carbon atoms or a radical having the formula:

$$-R''''\overset{R'}{\underset{R'''}{N}}R''SCN$$

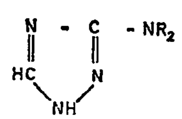
in which R'''' is a bridging polymethylene radical having from 2 to 4 carbon atoms, and R', R'' and R''' represent hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms,

B. From 0.04 to 2 weight percent of a polyhydroxy-substituted anthraquinone represented by the formula:



in which X, Y and Z each represent hydrogen or a hydroxyl group and at least one of these is a hydroxyl group, and

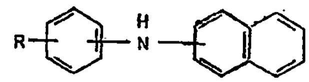
C. From 0.001 to 0.1 weight percent of a 3-amino-1H-1,2,4-triazole having the formula:



in which R is hydrogen or an alkyl radical having from 1 to 3 carbon atoms.

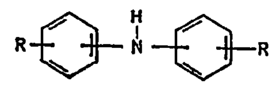
2. A lubricating oil composition as claimed in claim 1 containing from 0.05 to 0.5 weight percent of said ammonium thiocyanate, from 0.05 to 0.25 weight percent of said polyhydroxy-substituted anthraquinone, and from 0.003 to 0.05 weight percent of said 3-amino-1H-1,2,4-triazole.

3. A lubricating oil composition as claimed in claim 1 or 2 and additionally containing from 0.5 to 2.5 weight percent of a naphthylamine represented by the formula:



in which R is an alkyl or alkaryl radical having from about 4 to 12 carbon atoms.

4. A lubricating oil composition as claimed in any preceding claim and additionally containing from 0.5 to 2.0 percent of a dialkyldiphenylamine represented by the formula:



in which R is an alkyl radical having from 4 to 12 carbon atoms.

5. A lubricating oil composition as claimed in any preceding claim, and additionally containing from about 0.5 to 5 percent of a hydrocarbyl phosphate represented by the formula:

$$(RO)_3PO$$

in which R is a hydrocarbyl radical having from 2 to 12 carbon atoms.

6. A lubricating oil composition as claimed in claim 3 in which said naphthylamine is N-(*p*-*t*-octyl-phenyl)-$\alpha$-naphthylamine.

7. A composition as claimed in claim 4 in which said diphenylamine is p,p$^1$-di-tert.-octyldiphenylamine.

8. A composition as claimed in claim 5 in which said hydrocarbyl phosphate is tricresyl phosphate.

9. A lubricating oil composition as claimed in any preceding claim, in which said polyhydroxy-substituted anthraquinone is quinizarin or purpurin.

10. A lubricating oil composition as claimed in any preceding claim, in which said triazole is 3-methylamino-1H,-1,2,4-triazole or 3-amino-1H-1,2,4-triazole.

11. A lubricating oil composition as claimed in any of claims 1 to 9, in which said triazole is 3-ethylamino-1H-1,2,4-triazole or 3-dimethylamino-1H-1,2,4-triazole.

12. A lubricating oil composition as claimed in any preceding claim, in which said ammonium thiocyanate is N,N'-di-(tertiary-octyl)-1,2-ethanediammonium thiocyanate or diisobutylammonium thiocyanate.

13. A lubricating oil composition as claimed in any of claims 1 to 11, in which said ammonium thiocyanate is tert.-$C_{12-14}$ alkylammonium thiocyanate or N,N'-di-(tert.-$C_{18-22}$-alkyl)-1,2-ethanediammonium thio-

cyanate or bis-2-ethylhexylammonium thiocyanate.

14. A lubricating oil composition as claimed in claim 1 and substantially as hereinbefore described with reference to any of the Examples.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.